Determination of Consecutive Formation Constants of Complex Ions from Ion-Transfer Voltammetric Data

Hajime Katano* and **Mitsugi Senda**

Department of Bioscience, Faculty of Biotechnology, Fukui Prefectural University, Matsuoka, Yoshida, Fukui 910-11

(Received May 30, 1997)

The half-wave potentials of the voltammetric waves of facilitated transfer of Pb^{2+} ion by 1,4,7,10,13,16-hexathiacyclooctadecane across the nitrobenzene/water interface have been measured as a function of the concentration of free CH_3COO^- ion in aqueous phase. Using the equation of reversible half-wave ion-transfer potential, the formal formation constants of 1 : 1, 1 : 2, and 1 : 3 Pb^{2+}–CH_3COO^- complexes in the aqueous medium have been determined to be $10^{2.3}$ M^{-1}, $10^{3.0}$ M^{-2}, and $10^{4.0}$ M^{-3}, respectively. A polynomial regression method for the determination of the formation constants from voltammetric data is presented. Ion-transfer voltammetry at the liquid/liquid interface can be applied advantageously to the determination of consecutive formation constants of metal complexes with a ligand in aqueous media as well as those with an ionophore in organic media.

Ion-transfer voltammetry at the liquid/liquid or oil (O)/water (W) interface can be applied advantageously to the study of complex formation of metal ions with a ligand, usually belonging to the family of ionophores and present in O-phase. The fundamental principles on which these studies are based were first recognized by Koryta.[1] They have been applied to the facilitated transfer of alkaline metal ions and ammonium ion by dibenzo-18-crown-6 across the nitrobenzene (NB)/W interface, giving the formation constants of 1 : 1 complexes of these ions with dibenzo-18-crown-6 in NB solution.[2] Recently, the study has been extended to the cases where both 1 : 1 and 1 : 2 metal-ionophore complexes are formed in O-phase[3] and also to the cases when the ionophores are soluble in both O- and W-phases.[4]

In a previous paper,[5] using cyclic voltammetry and normal pulse voltammetry, the voltammetric behavior of facilitated transfer of Pb^{2+} ion by a macrocyclic polythiaether 1,4,7,10,13,16-hexathiacyclooctadecane (HTCO) across the NB/W interface has been shown to be a reversible process, assisted by the formation of an 1 : 1 Pb^{2+}–HTCO complex in NB-phase. Also, it has been shown that the half-wave potentials of the facilitated transfer of Pb^{2+} ion across the NB/W interface are shifted to more positive potential by the complex formation of Pb^{2+} ion with a ligand like acetate (CH_3COO^-) ion in W-phase, indicating that the ion-transfer voltammetry can be applied advantageously to the determination of the formation constants of complex ions also in aqueous media.

In this study, the half-wave potentials of the voltammetric waves of facilitated transfer of Pb^{2+} ion by HTCO across the NB/W interface have been measured as a function of the concentration of free CH_3COO^- ion in W-phase. Using the equation of the reversible half-wave potential of the facilitated ion-transfer across the O/W interface,[5] researchers have determined the formal formation constants of Pb^{2+}–CH_3COO^- complexes in the aqueous medium by the DeFord–Hume method in classical polarography with a dropping mercury electrode,[6] and also by the method of polynomial regression analysis referred to as least squares. Criteria for selecting a polynomial regression model have also been discussed.

Experimental

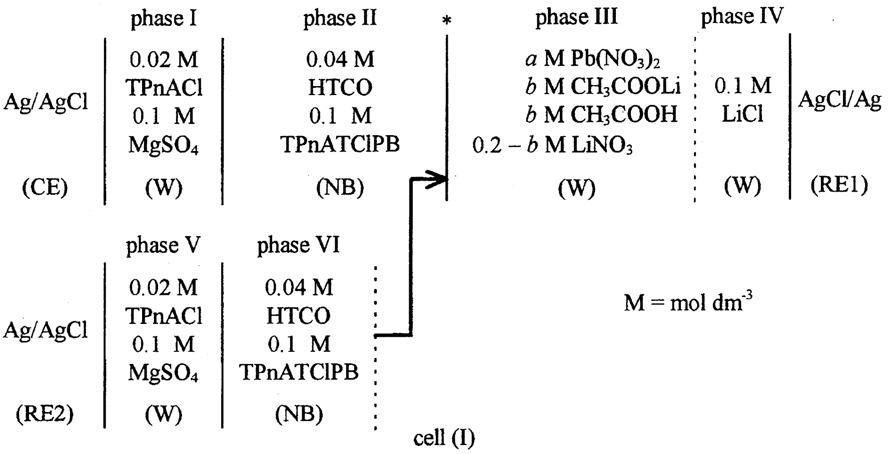
HTCO was obtained from Aldrich and used as received. *n*-Tetrapentylammonium tetrakis(4-chlorophenyl)borate (TPnATClPB) was prepared as described previously.[5] *n*-Tetrapentylammonium chloride (TPnACl) and NB were obtained from Wako and purified as described previously.[5] Other chemicals were of analytical grade and were used as received.

Facilitated transfer of Pb^{2+} ion by HTCO across the interface between NB and aqueous solutions was studied by means of cyclic voltammetry. The electrochemical system used for electrochemical measurements is represented by cell (I) (Chart 1). The polarizable NB/W interface, that is, the test interface, is indicated by an asterisk. The cell potential (E) is defined as the terminal potential of the reference electrode RE1 referred to that of RE2, and is related to the Galvani potential difference across the O/W interface ($\Delta_O^W \phi$) by

$$E = \Delta_O^W \phi + \Delta E_{ref}, \tag{1}$$

where ΔE_{ref} is determined by the reference electrode system consisting of RE1 and RE2 in cell (I). In this study, all the potentials are referred to the reversible half-wave potential for the transfer of tetramethylammonium (TMA^+) ion across the NB/W interface (${}_rE_{1/2,TMA}$), which was determined to be ${}_rE_{1/2,TMA}=0.369$ V using cell (I) with the test aqueous medium (phase III) containing 0.50 mM TMABr and 0.20 M $LiNO_3$ (1 M=1 mol dm^{-3}). The standard ion-transfer potential of TMA^+ ion is reported to be $\Delta_O^W \phi_{TMA}^0=0.035$ V.[7] Therefore, on appropriate assumptions,[8] ΔE_{ref} for cell (I) was determined to be $\Delta E_{ref}=0.325$ V.

The ionic strength (I) of the test aqueous medium was kept constant at I=0.2 by addition of $LiNO_3$. All measurements were carried out at 25±0.5°C. The details of the electrochemical measurements are described elsewhere.[5]



cell (I)

Chart 1.

Results and Discussion

Cyclic voltammograms for the facilitated transfer of Pb^{2+} ion by HTCO across the NB/W interface when the bulk concentration of the ionophore (L, here, HTCO) in NB-phase ($^*c_{\mathrm{L}}^{\mathrm{O}}=4.0\times10^{-2}$ M in this experiment) was much higher than the total concentration of a metal ion (M, here, Pb^{2+} ion) in the bulk of W-phase ($(^*c_{\mathrm{M}}^{\mathrm{W}})_{\mathrm{t}}=2.0\times10^{-4}$ M in this experiment) were recorded at different bulk concentrations of a hydrophilic ligand ($\mathrm{A_w}$, here, CH_3COO^- ion) in W-phase ($^*c_{\mathrm{Aw}}^{\mathrm{W}}$) which were changed from 5.0×10^{-3} to 1.6×10^{-1} M in this experiment. Typical examples are shown in Fig. 1. The anodic peak current (i_{pa}) corrected for the base current was proportional to $(^*c_{\mathrm{M}}^{\mathrm{W}})_{\mathrm{t}}$ between 2.5×10^{-5} and 4.0×10^{-4} M. i_{pa} was also proportional to the square root of scan rate (v) between 0.01 and 0.2 V s^{-1}. The anodic and cathodic peak potentials (E_{pa} and E_{pc}) and the midpoint potential (E_{mid}), defined by $E_{\mathrm{mid}}=(E_{\mathrm{pa}}+E_{\mathrm{pc}})/2$, were independent of v and $(^*c_{\mathrm{M}}^{\mathrm{W}})_{\mathrm{t}}$. The peak separation ($\Delta E_{\mathrm{p}}$), defined by $\Delta E_{\mathrm{p}}=E_{\mathrm{pa}}-E_{\mathrm{pc}}$, was $\Delta E_{\mathrm{p}}=33\pm2$ mV, which is close to the theoretical value of 28.5 mV for a reversible transfer of a divalent ion.[9] These results indicate that the facilitated transfer of Pb^{2+} ion by HTCO across the NB/W interface is reversible or nernstian, and is controlled by diffusion of Pb^{2+} ion species in W-phase toward the interface.

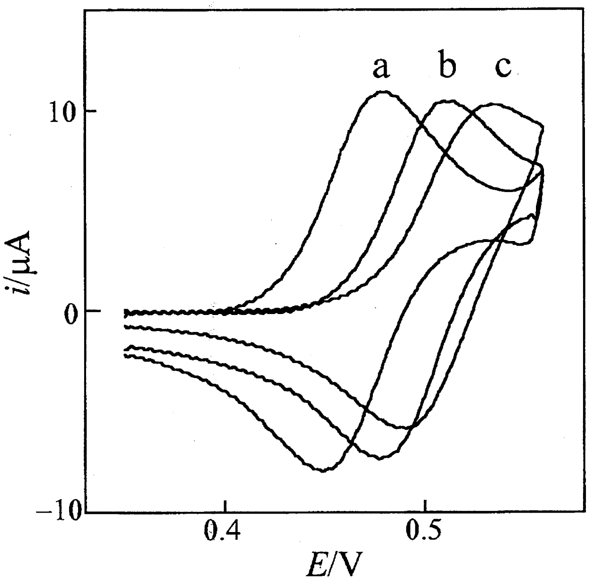


Fig. 1. Cyclic voltammograms for the facilitated transfer of Pb^{2+} ion by HTCO across the NB/W interface at different concentrations of CH_3COO^- ion in W-phase, $^*c_{\mathrm{Aw}}^{\mathrm{W}}$= a) 0, b) 6.0×10^{-2}, and c) 1.2×10^{-1} M, when $^*c_{\mathrm{L}}^{\mathrm{O}}=4.0\times10^{-2}$ M and $(^*c_{\mathrm{M}}^{\mathrm{W}})_{\mathrm{t}}=2.0\times10^{-4}$ M. Scan rate, 0.05 V s^{-1}.

The reversible half-wave potentials ($_{\mathrm{r}}E_{1/2}$) of the facilitated transfer of Pb^{2+} ion have been determined by taking $_{\mathrm{r}}E_{1/2}=E_{\mathrm{mid}}$.[9] When $^*c_{\mathrm{L}}^{\mathrm{O}}\gg(^*c_{\mathrm{M}}^{\mathrm{W}})_{\mathrm{t}}$ and $^*c_{\mathrm{Aw}}^{\mathrm{W}}\gg(^*c_{\mathrm{M}}^{\mathrm{W}})_{\mathrm{t}}$, $_{\mathrm{r}}E_{1/2}$ of facilitated transfer of M ion by L across the O/W interface can be given by Eq. 2.[5]

$$\begin{aligned}{}_{\mathrm{r}}E_{1/2} = {} & E_{\mathrm{M}}^{0\prime}+(RT/zF)\ln(\overline{D}_{\mathrm{M}}^{\mathrm{W}}/\overline{D}_{\mathrm{M}}^{\mathrm{O}})^{1/2}\\ & +(RT/zF)\ln\left[1+\sum_{j=1}^{n}K_{\mathrm{MAw}j}^{\mathrm{W}}(^*c_{\mathrm{Aw}}^{\mathrm{W}})^{j}\right]\\ & -(RT/zF)\ln\left[1+\sum_{p=1}^{m}K_{\mathrm{ML}p}^{\mathrm{O}}(^*c_{\mathrm{L}}^{\mathrm{O}})^{p}\right]\end{aligned}\tag{2}$$

Here, $E_{\mathrm{M}}^{0\prime}$ is the formal ion-transfer potential of M ion across the O/W interface; z is the number of charge of M ion including the sign; $K_{\mathrm{ML}p}^{\mathrm{O}}$ and $K_{\mathrm{MAw}j}^{\mathrm{W}}$ are the formal formation constants of the formation of complex species ML_p ($=\mathrm{M}+p\mathrm{L}$, $p=1,2,\cdots,m$) in O-phase and those of MAw_j ($=\mathrm{M}+j\mathrm{Aw}$, $j=1,2,\cdots,n$) in W-phase, respectively, as defined by

$$K_{\mathrm{ML}p}^{\mathrm{O}}=c_{\mathrm{ML}p}^{\mathrm{O}}/c_{\mathrm{M}}^{\mathrm{O}}(c_{\mathrm{L}}^{\mathrm{O}})^{p}\tag{3}$$

and

$$K_{\mathrm{MAw}j}^{\mathrm{W}}=c_{\mathrm{MAw}j}^{\mathrm{W}}/c_{\mathrm{M}}^{\mathrm{W}}(c_{\mathrm{Aw}}^{\mathrm{W}})^{j},\tag{4}$$

where c_i^{α} is the concentration of species i (=M, L, ML_p, Aw, or MAw_j) in α-phase (α=W or O); $\overline{D}_{\mathrm{M}}^{\mathrm{W}}$ and $\overline{D}_{\mathrm{M}}^{\mathrm{O}}$ are the average diffusion coefficients of M ion in W- and O-phase, defined in terms of the diffusion coefficients of species i (=M, L, ML_p, Aw, or MAw_j) in α-phase (α=W or O) (D_i^{α}) respectively, by

$$\overline{D}_{\mathrm{M}}^{\mathrm{W}}=\left(D_{\mathrm{M}}^{\mathrm{W}}+\sum_{j=1}^{n}D_{\mathrm{MAw}j}^{\mathrm{W}}K_{\mathrm{MAw}j}^{\mathrm{W}}(^*c_{\mathrm{Aw}}^{\mathrm{W}})^{j}\right)\Big/\left(1+\sum_{j=1}^{n}K_{\mathrm{MAw}j}^{\mathrm{W}}(^*c_{\mathrm{Aw}}^{\mathrm{W}})^{j}\right)\tag{5}$$

and

$$\overline{D}_{\mathrm{M}}^{\mathrm{O}} = (D_{\mathrm{M}}^{\mathrm{O}} + \sum_{p=1}^{m} D_{\mathrm{ML}p}^{\mathrm{O}} K_{\mathrm{ML}p}^{\mathrm{O}} ({}^{*}c_{\mathrm{L}}^{\mathrm{O}})^{p})/(1 + \sum_{p=1}^{m} K_{\mathrm{ML}p}^{\mathrm{O}} ({}^{*}c_{\mathrm{L}}^{\mathrm{O}})^{p}). \tag{6}$$

The anodic peak current of the facilitated transfer of M ion is given by[9)]

$$i_{\mathrm{pa}} = 0.4463 zFA\overline{D}_{\mathrm{M}}^{\mathrm{W}1/2} (zFv/RT)^{1/2} ({}^{*}c_{\mathrm{M}}^{\mathrm{W}})_{\mathrm{t}}. \tag{7}$$

In these theoretical Eqs. 2, 5, 6, and 7, it is assumed that L is so hydrophobic that the presence of L and ML_p in W-phase can be neglected, whereas $\mathrm{A_W}$ and $\mathrm{MA_{W\mathit{j}}}$ are so hydrophilic that the presence of $\mathrm{A_W}$ and $\mathrm{MA_{W\mathit{j}}}$ in O-phase can be neglected.

As stated above, the behavior of i_{pa} can be well explained by Eq. 7. The values of $\overline{D}_{\mathrm{M}}^{\mathrm{W}}$ calculated by use of Eq. 7 are plotted against ${}^{*}c_{\mathrm{Aw}}^{\mathrm{W}}$ on plot (a) in Fig. 2. A 95% confidence interval on the mean value of $\overline{D}_{\mathrm{M}}^{\mathrm{W}}$ was $(6.3\pm0.3)\times10^{-6}$ $\mathrm{cm^2\,s^{-1}}$. On plot (a) in Fig. 2, a slight decreasing in the values of $\overline{D}_{\mathrm{M}}^{\mathrm{W}}$ with increasing ${}^{*}c_{\mathrm{Aw}}^{\mathrm{W}}$ is observed. This may be explained by Eq. 5 on assuming that the formation of complexes of $\mathrm{Pb^{2+}}$ with $\mathrm{CH_3COO^-}$ ion in W-phase results in the decreasing of $D_{\mathrm{MAw}j}^{\mathrm{W}}$.

The observed values of ${}_{\mathrm{r}}E_{1/2}$ are plotted against ${}^{*}c_{\mathrm{Aw}}^{\mathrm{W}}$ on plot (b) in Fig. 2. The voltammetric data can be analyzed by the DeFord–Hume method in classical polarography[6)] using Eq. 2. We define the DeFord–Hume F_0 function for ion-transfer voltammetry as

$$\begin{aligned} F_0 &= (D_{\mathrm{M}}^{\mathrm{W}}/\overline{D}_{\mathrm{M}}^{\mathrm{W}})^{1/2} \exp[(zF/RT)({}_{\mathrm{r}}E_{1/2} - {}_{\mathrm{r}}E_{1/2}^{\mathrm{M}})] \\ &= 1 + \sum_{k=1}^{n} K_{\mathrm{MAw}k}^{\mathrm{W}} ({}^{*}c_{\mathrm{Aw}}^{\mathrm{W}})^{k}, \end{aligned} \tag{8}$$

where ${}_{\mathrm{r}}E_{1/2}^{\mathrm{M}}$ is the reversible half-wave potential of the facilitated transfer of the simple (aquo) ion, as given by

$$\begin{aligned} {}_{\mathrm{r}}E_{1/2}^{\mathrm{M}} &= E_{\mathrm{M}}^{0'} + (RT/zF)\ln(D_{\mathrm{M}}^{\mathrm{W}}/\overline{D}_{\mathrm{M}}^{\mathrm{O}})^{1/2} \\ &\quad -(RT/zF)\ln[1 + \sum_{p=1}^{m} K_{\mathrm{ML}p}^{\mathrm{O}} ({}^{*}c_{\mathrm{L}}^{\mathrm{O}})^{p}]. \end{aligned} \tag{9}$$

Then, we define, in general, the DeFord–Hume F_j-function (j=1,2,3,$\cdots$) as

$$\begin{aligned} F_j &= (F_{j-1} - \lim({}^{*}c_{\mathrm{Aw}}^{\mathrm{W}} \to 0)F_{j-1})/{}^{*}c_{\mathrm{Aw}}^{\mathrm{W}} \\ &= \sum_{k=j}^{n} K_{\mathrm{MAw}k}^{\mathrm{W}} ({}^{*}c_{\mathrm{Aw}}^{\mathrm{W}})^{k-j}, \end{aligned} \tag{10}$$

where $\lim({}^{*}c_{\mathrm{Aw}}^{\mathrm{W}}\to0)F_j$ denotes the value of F_j extrapolated to ${}^{*}c_{\mathrm{Aw}}^{\mathrm{W}}=0$, which is equal to $K_{\mathrm{MAw}j}^{\mathrm{W}}$, as can be seen from Eq. 10. Note that $\lim({}^{*}c_{\mathrm{Aw}}^{\mathrm{W}}\to0)F_0=1$.

In Fig. 3, F_1, F_2, and F_3 are plotted against ${}^{*}c_{\mathrm{Aw}}^{\mathrm{W}}$. The observed values of ${}_{\mathrm{r}}E_{1/2}=0.463$ V at ${}^{*}c_{\mathrm{Aw}}^{\mathrm{W}}=0$ and ${}^{*}c_{\mathrm{NO3}}^{\mathrm{W}}=0.20$ M, ${}^{*}c_{\mathrm{NO3}}^{\mathrm{W}}$ being the bulk concentration of $\mathrm{NO_3}^-$ ion in the W-phase, is used for ${}_{\mathrm{r}}E_{1/2}^{\mathrm{M}}$ as a preliminary value (see below) to evaluate F_0-function by Eq. 8. Also, $D_{\mathrm{M}}^{\mathrm{W}}=6.7\times10^{-6}$ $\mathrm{cm^2\,s^{-1}}$ as calculated by Eq. 7 from the peak height at ${}^{*}c_{\mathrm{Aw}}^{\mathrm{W}}=0$ and ${}^{*}c_{\mathrm{NO3}}^{\mathrm{W}}=0.20$ M, and $\overline{D}_{\mathrm{M}}^{\mathrm{W}}=6.3\times10^{-6}$ $\mathrm{cm^2\,s^{-1}}$ (see above) are employed. The extrapolation of $\lim({}^{*}c_{\mathrm{Aw}}^{\mathrm{W}}\to0)F_j$ was determined by linear regression analysis referred to as least squares. Thus, the regression line fitted to the F_1 vs. ${}^{*}c_{\mathrm{Aw}}^{\mathrm{W}}$ plot in the range of ${}^{*}c_{\mathrm{Aw}}^{\mathrm{W}}$ between 5.0×10^{-3} and 4.0×10^{-2} M is given as

$$\tilde{F}_1/\mathrm{M}^{-1} = (137\pm20) + (732\pm284)({}^{*}c_{\mathrm{Aw}}^{\mathrm{W}}/\mathrm{M}), \tag{11}$$

which is shown by the dashed line on plot (a) in Fig. 3.

As seen in plot (b) in Fig. 3, the F_2 vs. ${}^{*}c_{\mathrm{Aw}}^{\mathrm{W}}$ plot is likely to be linear in the range of ${}^{*}c_{\mathrm{Aw}}^{\mathrm{W}}$ between 6.0×10^{-2} and 1.2×10^{-1} M. As a measure of the linear relationship, the coefficient of determination (r^2), defined by[10)]

$$r^2 = 1 - SS_{\mathrm{E}}/S_{yy}, \tag{12}$$

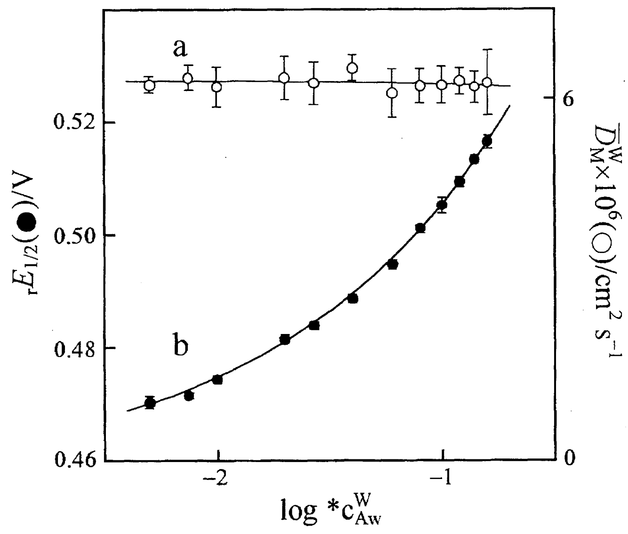


Fig. 2. Plots of a) $\overline{D}_{\mathrm{M}}^{\mathrm{W}}$ and b) ${}_{\mathrm{r}}E_{1/2}$ against $\log {}^{*}c_{\mathrm{Aw}}^{\mathrm{W}}$. The vertical bars indicate the 95% confidence intervals. The solid line (b) is the calculated value of ${}_{\mathrm{r}}E_{1/2}$ by Eq. 2 on $K_{\mathrm{MAw}}^{\mathrm{W}}=10^{2.1}$ $\mathrm{M^{-1}}$, $K_{\mathrm{MAw2}}^{\mathrm{W}}=10^{2.8}$ $\mathrm{M^{-2}}$, and $K_{\mathrm{MAw3}}^{\mathrm{W}}=10^{3.8}$ $\mathrm{M^{-3}}$.

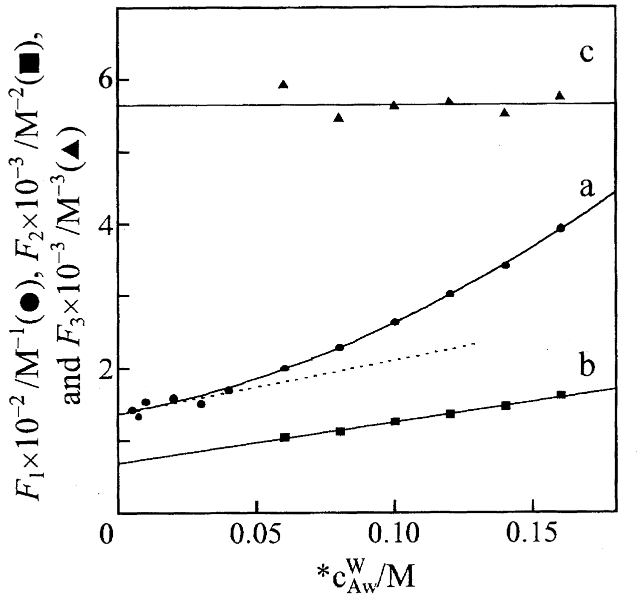


Fig. 3. Plots of a) F_1, b) F_2, and c) F_3 against ${}^{*}c_{\mathrm{Aw}}^{\mathrm{W}}$. The solid lines are the calculated values by Eq. 10 on $K_{\mathrm{MAw}}^{\mathrm{W}}=10^{2.1}$ $\mathrm{M^{-1}}$, $K_{\mathrm{MAw2}}^{\mathrm{W}}=10^{2.8}$ $\mathrm{M^{-2}}$, and $K_{\mathrm{MAw3}}^{\mathrm{W}}=10^{3.8}$ $\mathrm{M^{-3}}$.

is often used. Here, SS_{E} and S_{yy} are the error sum of squares and total corrected sum of squares, respectively, defined by

$$SS_{\mathrm{E}} = \sum_{k=1}^{M}(F_{j,k} - \tilde{F}_{j,k})^2 \tag{13}$$

and

$$S_{yy} = \sum_{k=1}^{M}(F_{j,k}^2) - (\sum_{k=1}^{M} F_{j,k})^2/M, \tag{14}$$

where M is the number of sets of data fitted. Thus, the regression line for the plot (b) in Fig. 3 is given as

$$\tilde{F}_2/\mathrm{M}^{-2} = (684 \pm 73) + (5646 \pm 642)(^*c_{\mathrm{Aw}}^{\mathrm{W}}/\mathrm{M}) \tag{15}$$

with r^2=0.995, indicating a strong linear relationship between F_2 and $^*c_{\mathrm{Aw}}^{\mathrm{W}}$. Therefore, the *last* complex is determined to be 1 : 3 complex (here, $\mathrm{Pb(CH_3COO)_3}^-$), that is, n=3, in the range of $^*c_{\mathrm{Aw}}^{\mathrm{W}}$ studied.

The F_3 function (plot (c) in Fig. 3) seems to be parallel with $^*c_{\mathrm{Aw}}^{\mathrm{W}}$, as expected. A 95% confidence interval on the mean value of F_3 is 6793±342 M^{-3}. Thus, the formal formation constants of $K_{\mathrm{MAw}}^{\mathrm{W}}$, $K_{\mathrm{MAw2}}^{\mathrm{W}}$, and $K_{\mathrm{MAw3}}^{\mathrm{W}}$ are determined to be $10^{2.1\pm0.1}$ M^{-1}, $10^{2.8\pm0.1}$ M^{-2}, and $10^{3.8\pm0.1}$ M^{-3}, respectively. The calculated values of F_j (j=1, 2, and 3) with these $K_{\mathrm{MAw}j}^{\mathrm{W}}$-values are shown by the solid lines in Fig. 3.

The voltammetric data of F_0- or F_1-function can be directly analyzed, instead of applying the classical DeFord–Hume method as described above, by polynomial regression analysis referred to as least squares. Linear, quadratic, cubic, quartic, and 5th equations were fitted to sets of F_1 vs. $^*c_{\mathrm{Aw}}^{\mathrm{W}}$ plot in Fig. 3. An important problem in applications of the polynomial regression analysis involves selecting the order of polynomial regression equation. For this study, three criteria can be used for evaluating and comparing the different polynomial regression models. The first criterion is to consider the mean square error (MS_{E}), defined by[10)]

$$MS_{\mathrm{E}} = SS_{\mathrm{E}}/(M - N), \tag{16}$$

where N is the order of polynomial regression equation. The second criterion is the adjusted r^2 ($\bar{r}^2$), defined by[10)]

$$\bar{r}^2 = 1 - ((M-1)/(M-N))(1-r^2). \tag{17}$$

The third criterion is Akaike's Information Criterion (AIC), defined by[11)]

$$AIC = M \ln SS_{\mathrm{E}} + 2N. \tag{18}$$

The logical criteria are to choose the order of the polynomial regression model so that MS_{E} is minimum, $\bar{r}^2$ is maximum, or AIC-value is minimum. A polynomial regression software equipped for the output of the criteria and confidence intervals of regression coefficients was programmed with C++ language in this laboratory. Table 1 represents the results of running polynomial regressions. The quadratic model is definitely superior with respect to the MS_{E} criterion. This model also results in a maximum $\bar{r}^2$ and a minimum AIC-value. Therefore, we selected the quadratic model as the "best" regression equation, which is expressed by

Table 1. Results of Running Polynomial Regressions for F_1 vs. $^*c_{\mathrm{Aw}}^{\mathrm{W}}$ Plot

Equation	MS_{E}	$\bar{r}^2$	AIC-value
Linear	232	0.9694	97.0
Quadratic	39	0.9948	76
Cubic	43	0.9942	78
Quartic	47	0.9937	80
5th	53	0.9930	81

$$(\tilde{F}_1/\mathrm{M}^{-1}) = (138 \pm 9) + (632 \pm 307)(^*c_{\mathrm{Aw}}^{\mathrm{W}}/\mathrm{M}) \\ +(6068 \pm 1930)(^*c_{\mathrm{Aw}}^{\mathrm{W}}/\mathrm{M})^2 \tag{19}$$

The result indicates again that n=3. Thus, $K_{\mathrm{MAw}}^{\mathrm{W}}$, $K_{\mathrm{MAw2}}^{\mathrm{W}}$, and $K_{\mathrm{MAw3}}^{\mathrm{W}}$ are determined to be $10^{2.1\pm0.0}$ M^{-1}, $10^{2.8\pm0.2}$ M^{-2}, and $10^{3.8\pm0.1}$ M^{-3}, respectively. The calculated values of $_{\mathrm{r}}E_{1/2}$ by Eq. 2 on the $K_{\mathrm{MAw}j}^{\mathrm{W}}$-values are shown by solid line (b) in Fig. 2. Agreement of the calculated values with the experimental values is excellent with 0.2 mV of 95% confidence limit.

Usually, the determination of the formation constants of metal complexes is made by use of perchlorate media. In the present study, however, a nitrate medium was used, because the current due to the transfer of perchlorate ion across the NB/W interface is superimposed on that of Pb^{2+} ion, which may interfere with accurate determination of the transfer current of Pb^{2+} ion. In aqueous media, Pb^{2+} ion is known to form a 1 : 1 complex with NO_3^- ion with the thermodynamic formation constant of $10^{1.08}$ M^{-1}.[12)] Then, the formal formation constant, $K_{\mathrm{MNO3}}^{\mathrm{W}}$, at I=0.2 may be calculated to be $10^{0.47}$ M^{-1} using Devies's equation.[13)] On assuming both $^*c_{\mathrm{Aw}}^{\mathrm{W}} \gg (^*c_{\mathrm{M}}^{\mathrm{W}})_{\mathrm{t}}$ and $^*c_{\mathrm{NO3}}^{\mathrm{W}} \gg (^*c_{\mathrm{M}}^{\mathrm{W}})_{\mathrm{t}}$, the third term in the right-hand side of Eq. 2 should be modified to $(RT/zF)\ln[1+K_{\mathrm{MNO3}}^{\mathrm{W}}\,^*c_{\mathrm{NO3}}^{\mathrm{W}}+\sum_{j=1}^{n}K_{\mathrm{MAw}j}^{\mathrm{W}}(^*c_{\mathrm{Aw}}^{\mathrm{W}})^j]$. In Eq. 2, $\overline{D}_{\mathrm{M}}^{\mathrm{W}}$ should be modified accordingly (see Eq. 5). Therefore, the reversible half-wave potential when $^*c_{\mathrm{Aw}}^{\mathrm{W}}$=0 ($_{\mathrm{r}}E_{1/2}'$) is given by

$$_{\mathrm{r}}E_{1/2}' = {_{\mathrm{r}}E_{1/2}^{\mathrm{M}}} + (RT/zF)\ln(\overline{D}_{\mathrm{M}}^{\mathrm{W}\prime}/D_{\mathrm{M}}^{\mathrm{W}})^{1/2} \\ +(RT/zF)\ln(1 + K_{\mathrm{MNO3}}^{\mathrm{W}}\,^*c_{\mathrm{NO3}}^{\mathrm{W}}{}'), \tag{20}$$

where $^*c_{\mathrm{NO3}}^{\mathrm{W}}{}'$ is the bulk concentration of $\mathrm{NO_3}^-$ ion in the W-phase when $^*c_{\mathrm{Aw}}^{\mathrm{W}}$=0 and $\overline{D}_{\mathrm{M}}^{\mathrm{W}\prime}$ the average diffusion coefficients of species i (=M and $\mathrm{MNO_3}$) in W-phase when $^*c_{\mathrm{Aw}}^{\mathrm{W}}$=0, defined by

$$\overline{D}_{\mathrm{M}}^{\mathrm{W}\prime} = (D_{\mathrm{M}}^{\mathrm{W}} + D_{\mathrm{MNO3}}^{\mathrm{W}}K_{\mathrm{MNO3}}^{\mathrm{W}}\,^*c_{\mathrm{NO3}}^{\mathrm{W}}{}')/(1 + K_{\mathrm{MNO3}}^{\mathrm{W}}\,^*c_{\mathrm{NO3}}^{\mathrm{W}}{}'). \tag{21}$$

Thus, F_1-function defined by Eq. 10 at j=1 can be corrected as

$$F_1' = \{(\overline{D}_{\mathrm{M}}^{\mathrm{W}\prime}/\overline{D}_{\mathrm{M}}^{\mathrm{W}})^{1/2}\exp[(zF/RT)(_{\mathrm{r}}E_{1/2} - {_{\mathrm{r}}E_{1/2}'})] - 1\} \\ /^*c_{\mathrm{Aw}}^{\mathrm{W}} = \sum_{k=1}^{n}K_{\mathrm{app},k}^{\mathrm{W}}(^*c_{\mathrm{Aw}}^{\mathrm{W}})^{k-1}, \tag{22}$$

where F_1' is the F_1-function corrected for the formation of $\mathrm{PbNO_3}^+$ complex. Since $^*c_{\mathrm{NO3}}^{\mathrm{W}} + {^*c_{\mathrm{Aw}}^{\mathrm{W}}} = {^*c_{\mathrm{NO3}}^{\mathrm{W}}}'$ (see Experimental), the apparent formal formation constants ($K_{\mathrm{app},j}^{\mathrm{W}}$) in Eq. 22 is given for j=1 by

Table 2. Formal Formation Constants of Pb^{2+}–CH_3COO^- Complexes

	$\log K^W_{MAw}$	$\log K^W_{MAw2}$	$\log K^W_{MAw3}$
DeFord–Hume method	2.1 ± 0.1	2.8 ± 0.1	3.8 ± 0.1
Polynoninal reglession	$2.1_4 \pm 0.0_3$	2.8 ± 0.2	3.8 ± 0.1
After correction for the formation of $PbNO_3$	$2.3_5 \pm 0.0_3$	3.0 ± 0.2	4.0 ± 0.1
Ref. 14	2.2	2.9	3.5

$$K^W_{app,1} = (K^W_{MAw} - K^W_{MNO3})/(1 + K^W_{MNO3}\,{}^*c^W_{NO3}{}') \tag{23}$$

and for $j > 1$ by

$$K^W_{app,j} = K^W_{MAwj}/(1 + K^W_{MNO3}\,{}^*c^W_{NO3}{}') \tag{24}$$

When ${}_rE_{1/2}{}'=0.463$ V, $\overline{D}^{W\prime}_M = 6.7\times10^{-6}$ cm^2 s^{-1}, and $\overline{D}^W_M = 6.3\times10^{-6}$ cm^2 s^{-1} (see above) are employed, F'_1 is numerically equal to F_1 of plot (a) in Fig. 3. Therefore, $K^W_{app,1}$, $K^W_{app,2}$, and $K^W_{app,3}$ are calculated to be 138 ± 9 M^{-1}, 632 ± 307 M^{-2}, and 6068 ± 1930 M^{-3}, respectively, by the polynomial regression analysis, as described above. Using Eqs. 23 and 24 with $K^W_{MNO3}=10^{0.47}$ M^{-1} and ${}^*c^W_{NO3}{}'=0.20$ M, K^W_{MAw1}, K^W_{MAw2}, and K^W_{MAw3} were calculated to be 222 ± 14 M^{-1}, 1005 ± 488 M^{-2}, and 9648 ± 3069 M^{-3}, respectively.

The K^W_{MAwj}-values obtained in this study are summarized in Table 2. The values obtained by DeFord–Hume method and those by polynomial regression analysis are in fair agreement with each other. The corrected values are 0.2 larger than uncorrected ones. However, the differences of the K^W_{MAw2}- and K^W_{MAw3}-values are not significant at 95% confidence level. The reported values in perchlorate medium (I=1.98) by polarography with a dropping mercury electrode[14] are also listed in Table 2. The results are in reasonable harmony with the reported ones.

Other metal ions, such as Cd^{2+} and Cu^{2+} ions, also give well-defined ion-transfer voltammograms facilitated by polythiaethers at the O/W interface.[5] The determination of formation constants of other metal complex ions will be published elsewhere. In conclusion, ion-transfer voltammetry at the liquid/liquid interface can be advantageously applied to the determination of the consecutive formation constants of metal complexes with a ligand in aqueous media as well as that with an ionophore in organic media.

This work was supported by a Grant-in-Aid from Fukui-ken University Science Foundation, to which the authors (H.K. and M.S.) are very grateful.

References

1) J. Koryta, *Ion-Sel. Electrodes Rev.*, **5**, 131 (1983).
2) M. Senda, T. Osakai, T. Kakutani, and T. Kakiuchi, *Nippon Kagaku Kaisi*, **1986**, 956.
3) T. Kakiuchi and M. Senda, *J. Electroanal. Chem.*, **300**, 431 (1991); T. Kakiuchi, *J. Electroanal. Chem.*, **345**, 191 (1993).
4) H. Matsuda, Y. Yamada, K. Kanamori, Y. Kudo, and Y. Takeda, *Bull. Chem. Soc. Jpn.*, **64**, 1497 (1991).
5) H. Katano and M. Senda, *Anal. Sci.*, **12**, 683 (1996).
6) D. D. DeFord and D. N. Hume, *J. Am. Chem. Soc.*, **73**, 5321 (1951).
7) J. Koryta, P. Vanýsek, and M. Brezina, *J. Electroanal. Chem.*, **75**, 211 (1977).
8) T. Kakutani, T. Osakai, and M. Senda, *Bull. Chem. Soc. Jpn.*, **56**, 991 (1983).
9) R. S. Nicolson and I. Shain, *Anal. Chem.*, **36**, 706 (1964).
10) D. C. Montgomery and G. C. Runger, "Applied Statistics and Probability for Engineers," John Wiley and Sons, New York (1994).
11) H. Akaike, *Suri Kagaku*, **153**, 5 (1976).
12) A. A. Vlcek, *Collect. Czech. Chem. Commun.*, **20**, 400 (1955).
13) R. A. Robinson and R. H. Stokes, "Electrolyte Solutions," Butterworth, London (1959).
14) E. A. Burns and D. N. Hume, *J. Am. Chem. Soc.*, **78**, 3958 (1956).